

# A unique wavelength-dispersive soft X-ray emission spectrometer for electron probe X-ray microanalyzers

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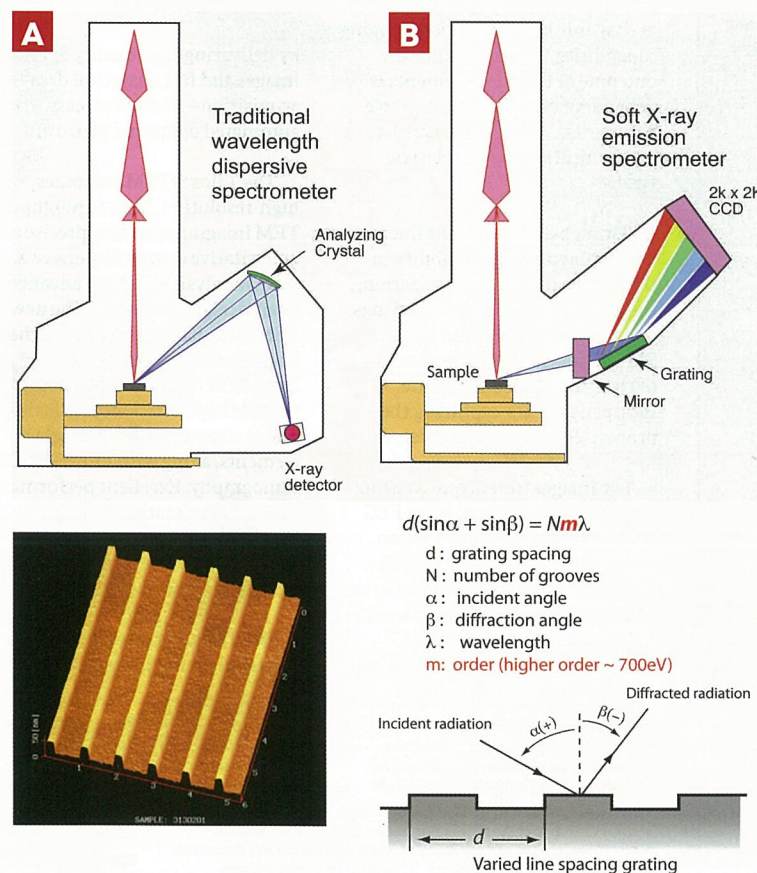
## INTRODUCTION

Wavelength-dispersive spectrometers (WDS) have been around for over 60 years. Their longevity is a testament to their effectiveness at measuring X-rays reproducibly, with high efficiency, and with very high energy spectral resolution. The spectrometers have two main components: (1) an analyzing crystal that diffract X-rays conforming to Bragg's Law ( $n\lambda = 2d \sin\theta$ ; where  $\lambda$  is the wavelength,  $d$  is the lattice spacing, and  $\theta$  is the incident angle of the X-ray); and (2) a counter that records each diffracted X-ray (Figure 1A).

The analyzing crystal and counter have to be moved synchronously to a new position for each different X-ray wavelength. This changes the incident angle of the X-ray striking the analyzing crystal, diffracting a different X-ray wavelength, and insuring that diffracted X-rays enter the counter.

Each analyzing crystal is only able to diffract a certain range of X-ray wavelengths (or energies). Three analyzing crystals (TAP, PET and LIF) are required to diffract the range of X-rays with energies between 0.5 and 14 keV. For lower energy X-rays, layered synthetic microstructures are available. These are constructed of interlayers of high and low atomic number materials on a scale of 6–20 nm. These in turn diffract long-wavelength (low-energy) X-rays, just as the natural crystalline material does for the short-wavelength (high-energy) X-rays. Using layered synthetic microstructures, one can analyze X-rays down to the Be K $\alpha$  line (~109 eV).

Even though wavelength-dispersive spectroscopy has been around for over 60 years, it is still the preferred X-ray analytical system for many,



because of its high spectral resolution. For comparison, an energy dispersive spectrometer (EDS) has an energy resolution of around 130 eV (when measured as the FWHM of Mn K $\alpha$ ) as compared to a traditional wavelength-dispersive spectrometer (WDS), which has an energy resolution of around 16 eV, almost an order of magnitude improvement.

## SOFT X-RAY EMISSION SPECTROMETER

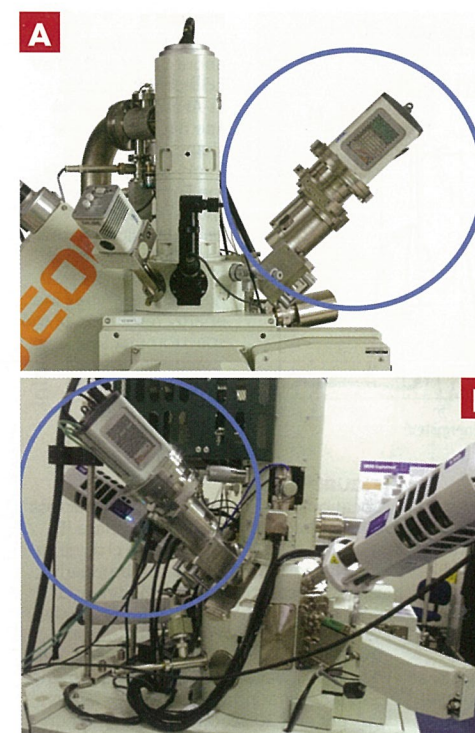
A powerful new wavelength-dispersive spectrometer has recently been developed for ultralow-energy X-rays. This new soft X-ray emission spectrometer (SXES) allows for X-rays with energies as low as 50 eV to be measured, which allows for the detection of X-rays as low as the Li K $\alpha$  line. It has an energy resolu-

**FIGURE 1**

Schematics of a traditional wavelength-dispersive spectrometer (WDS) (A) and the new wavelength-dispersive soft X-ray emission spectrometer (WD-SXES) (B). The traditional WDS uses an analyzing crystal to diffract X-rays of a particular wavelength into the detector. The WD-SXES uses a mirror to focus the X-rays onto a variable line-spacing grating, which disperses the X-rays into a spectrum that is projected onto a CCD array to be recorded

**FIGURE 2**

(A) Atomic force microscope image of a very small segment of an aberration-corrected, concave, variable line-spacing grating. (B) The conditions under which diffraction will occur



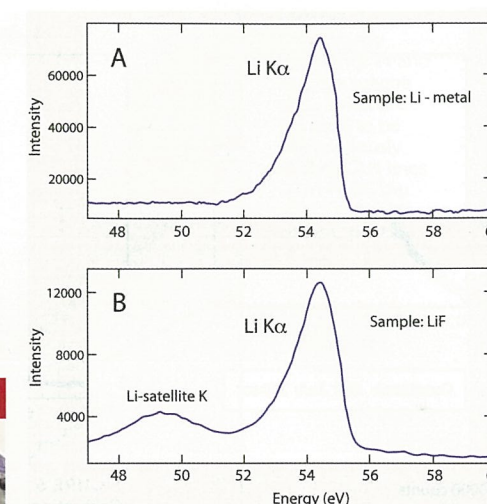
**FIGURE 3**

Examples of the WD-SXES system mounted on a JEOL electron probe microanalyzer (A), and a field-emission scanning electron microscope (B)

tion better than the traditional WDS, and detection sensitivity that allows for the measurement of boron even in the tens of parts per million range. Its design is a radical departure from the traditional WDS systems.

This new wavelength-dispersive spectrometer to detect ultrasoft X-rays was first designed and developed for transmission electron microscopes by Terauchi *et al.* [1]. Instead of using an analyzing crystal as the wavelength-dispersive element (Figure 1A), it uses a grating which has a variable spacing between its lines (Figure 1B). This aberration-corrected, concave, variable line-spacing grating (Figure 2) causes a range of X-rays to become dispersed based on their wavelengths, where they are then projected onto a charge-coupled device (CCD) that acts as the detector [2]. The result is a solid-state spectrometer that is able to collect an entire spectrum, simultaneously, without having to move either the grating or the detector. The success of this earlier WD-SXES for the TEM led to the development of a new WD-SXES that works with a range of JEOL's electron probe microanalyzers (EPMA's) (JXA-8100, JXA-8500F, JXA-8230 and JXA-8530F), and two scanning electron microscopes (SEMs) (JSM-7800F and JSM-7100F) (Figure 3).

Soft X-rays are inherently problematic because of their low efficiency of emission and difficulty of detection. This can be partially overcome by installing the WD-SXES on an EPMA or a similar high beam-current SEM. Typically these instruments can achieve over one microamp of beam current, resulting in much higher X-ray emission. A soft X-ray mirror is added to



**FIGURE 4**

Lithium K $\alpha$  spectra from Li metal (A) and LiF (B). The operating conditions used were a 100 nA of beam current, and 150 seconds of total acquisition time for both spectra, and a 15 kV accelerating voltage for the Li metal and a 5 kV accelerating voltage for the LiF.

the WD-SXES system to allow for more of the generated X-rays to be focused onto the grating, thereby improving its efficiency.

Two gratings have been developed for the WD-SXES, the JS50XL and the JS200N. The JS50XL works over the energy range of 50 to 170 eV, and the JS200N works over the energy range of 70 to 210 eV. Both gratings are set in one channel, as a pair, for the EPMA and SEM spectrometers, resulting in an energy range of 50 to 210 eV for these WD-SXES systems. This energy range includes the Li-K (54 eV), Al-L (72 eV), Si-L (92 eV), P-L (119 eV) and B-K (182 eV) X-ray lines. However, the variable line-spacing grating is also very efficient at dispersing higher-order X-ray lines. As a result, X-rays lines up to 700 eV can routinely be measured. This means that the K emission from C, N, O, and F; the L emission from Ti, V, Cr, Mn, and Fe; the M emission from Zr, Nb, Mo, Ag, Cd, Sn and Sb, and the N emissions from Hf, Ta, W, Re, Pt, Au, Bi and a few of the Lanthanides, such as U, can successfully be used for analyses.

Because the grating and CCD detector are rigidly fixed, with no moving parts, spectra are extremely reproducible. Likewise, hyperspectral data can be collected simultaneously, just like in SDD energy-dispersive spectroscopy, but with orders of magnitude better energy resolution. This parallel collection of the spectra allows for the acquisition of a spectral map, from which element maps and chemical-state maps can be extracted [2]. The size of the analytical area can vary from micrometers to millimeters in the EPMA and SEM. When stage scanning is used in the

EPMA, an area as large as 90 mm x 90 mm can be analyzed.

The ability of the WD-SXES to measure ultralow-energy X-rays, its extremely high energy resolution, and its exceptional sensitivity for soft X-rays, makes it an ideal spectrometer for both fundamental research on the chemical structure of valance electrons and compounds, and also for routine analyses of some of the most challenging elements and materials.

## APPLICATIONS

### EMISSION SPECTRA OF LITHIUM AND LITHIUM COMPOUNDS

Lithium is both an extremely challenging element to analyze and a very important component in lithium-ion batteries. The WD-SXES is capable of measuring energies low enough that spectrum from the Li K $\alpha$  peak can be clearly delineated at around 54 eV (Figure 4a). Similarly, the Li K $\alpha$  line and Li-satellite-K peak can be delineated from LiF (Figure 4b). The Li-satellite-K peak is very important in lithium-ion battery research because it can be used to monitor the chemical state of lithium in the anode. The height of this peak is very sensitive to the charge of the battery [2].

The intensity of the Li K $\alpha$  peak significantly diminishes as higher atomic elements form more of the matrix around the lithium atoms. Figure 5 shows the Li K $\alpha$  and Al L X-ray lines from a 5%Li-Al alloy. The Li K $\alpha$  peak is greatly reduced. However, even under these conditions, within this alloy, the calculated detection limits for lithium would be about 40 ppm (using a 1-sigma cut-off).

### WD-SXES ENERGY RESOLUTION

The aluminum L spectrum can be used to measure the energy resolution of the WD-SXES (Figure 5). The shape of the Al-L spectrum reflects the physics of its X-ray generation. The leading edge (high-energy side) represents the Fermi-edge of the Al L line, which has a fixed energy value and therefore should be perfectly vertical. The degree to which it slopes is a measure of the energy resolution of the spectrometer. Using this technique, the WD-SXES energy resolution can be measured at 0.2 eV. The characteristic shape of the Al line to the left (low-energy) side of the Fermi-edge corresponds to the density of state of the valance band [2].

### TRACE ELEMENT ANALYSES IN STEEL

Measuring trace elements in steel is very important in steel production. The higher atomic number elements can be measured routinely, but the light elements become significantly more difficult. Measuring nitrogen with much sensitivity is one of the most difficult. The problems are many including low efficiency N-K $\beta$  emission, preferential



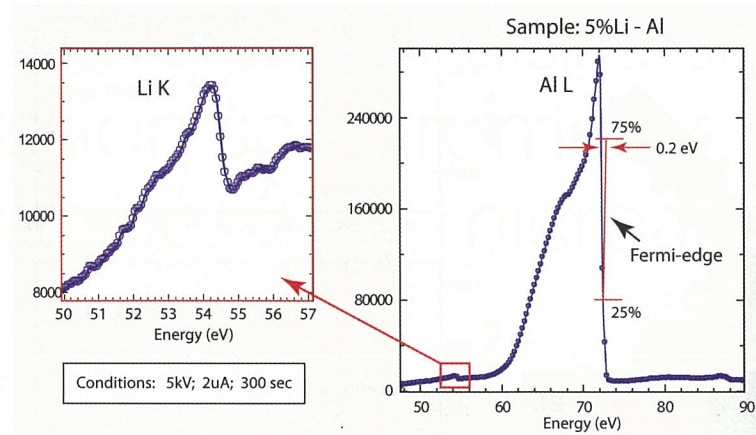
absorption by the detector windows in WDS systems, and massive peak overlaps in EDS systems. The WD-SXES has great potential for analyzing trace elements in steel. It has a better peak to background ratio, and its higher energy resolution produces a spectrum where the target peak are well separated from any potential overlaps. Preliminary experiments have shown that the B  $K\alpha$ , C  $K\alpha$  2nd order and N  $K\alpha$  2nd order can be observed unambiguously, with no peak overlaps [2]. Calibration curves derived for these three trace elements from 6 well established steel standards are linear, and show that concentrations as low as 10 ppm to 100 ppm in mass can be detected. Figure 6 shows an example of such a calibration curve for nitrogen. All of the six standards as well aligned along the linear regression curve. The results of this preliminary work suggest that a similar method could be used for trace element analyses in semiconductors.

#### CHARACTERIZING NON-STOICHIOMETRIC TiC-TiN COMPOUNDS

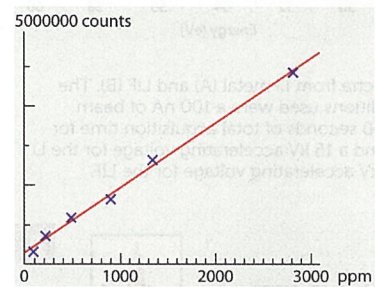
Titanium carbide and titanium nitride inclusions are a common concern in Ti based alloys, such as the shaped memory metal nitinol. These brittle inclusions can be the initiation points for crack propagation. Characterizing these inclusions can be very difficult. Non-stoichiometric titanium nitrides are extremely difficult to analyze with accuracy due to the complete overlap between the N  $K\alpha$  and the Ti  $L\alpha$  X-ray peaks. Using a standard light element analyzing crystal on a traditional WDS, the two lines are indistinguishable. However, on the WD-SXES the two lines are clearly distinguishable and can be deconvoluted with confidence.

Figure 7 shows an example of such a system. The dark grains are non-stoichiometric TiC-TiN phases (Figure 7A). A WD-SXES spectrum at the center of one such grain and one at its rim show distinctly different profiles representing changes in the Ti and N concentration (Figure 7C). Each profile shows a separate peak for the Ti and N, but clearly shows a change in the relative abundance. This is confirmed from the line profile data. A line profile across the center of such a grain shows the core is closer to the TiC composition and the rim is closer to the TiN composition (Figure 7B). For comparison, a spectrum for TiN is shown (Figure 7D) that was collected using a traditional wavelength-dispersive spectrometer with a light element analyzing crystal LDE1 (~6 nm d-spacing). The two X-ray lines for Ti and N are completely merged together into a single peak.

LOW-KV ANALYSES AND HIGHER ATOMIC NUMBER X-RAY LINES  
The advent of the field-emission elec-

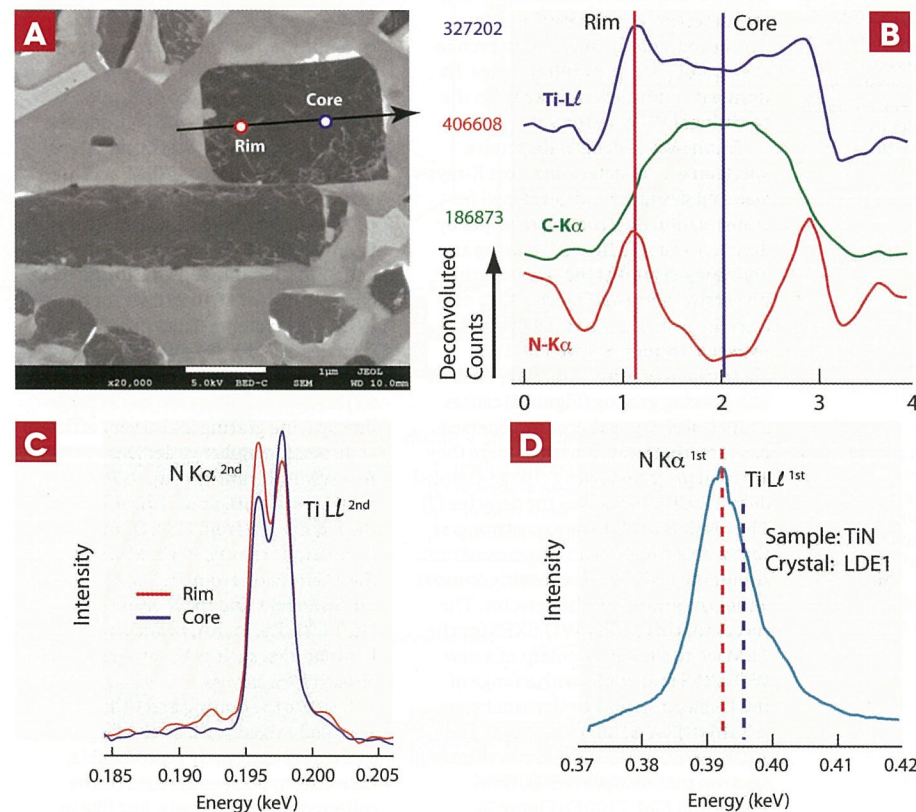


**FIGURE 5**  
A spectrum between about 50 eV and 90 eV collected from a 5% Li-Al alloy. The Al  $L\alpha$  line has a distinctive shape. The leading (high-energy) edge is the Fermi-edge, which should be vertical. Using the slope of this edge, as measured at the 25% and 75% peak height, determines the energy resolution of the spectrometer.



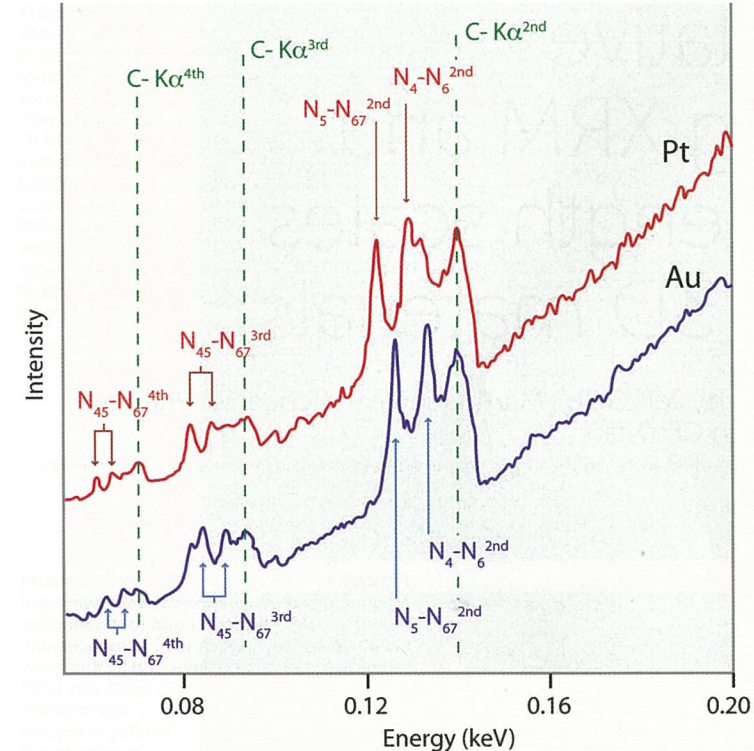
**FIGURE 6**  
Calibration curve for nitrogen in steel with a very linear correlation between counts and concentration showing that nitrogen can be measured down to at least 100 ppm. Operating conditions: 3 kV, 200 nA, and a dwell time of 100 seconds.

**FIGURE 7**  
Location image (A) and line profile across a non-stoichiometric TiC-TiN phase (B). (Data from Dr S. Asahina). The change in the Ni and Ti abundance can be clearly seen in spectra collected at the rim and core of the grain (C). The high-resolution WD-SXES can separate the Ni  $K\alpha$  from the Ti  $L\alpha$  peaks, which is not possible with traditional WDS (D). Operating conditions: 5 kV accelerating voltage, 35 nA beam current and 30 seconds dwell time per point



tron probe microanalyzer (FE-EPMA) has led the push to analyze smaller and smaller features. It is now possible to quantitatively analyze features in the 200 nm range [3]. To achieve this, lower accelerating voltages are required. This reduces the size of the electron interaction volume, which results from electron scatter within the sample. However,

working at lower accelerating voltages reduces the number of X-ray lines that can be used for the analysis. The higher energy X-ray lines are not generated when lower accelerating voltages are used. This becomes a problem if one is using EDS because of the resulting massive peak overlaps in the low energy region of the spectrum. Even with WDS,



**FIGURE 8**  
Low-energy spectra for Pt and Au. The spectra show what are believed to be not previously described N lines from Pt and Au along with high order C peaks.

this can be a problem for some elements. The new WD-SXES may open up great new opportunities for low kV analyses because of its high spectral resolution at the very low keV range.

New, very detailed, spectral data are being collected on the very low-energy X-ray line from the higher atomic elements. Because of the higher energy resolution of the WD-SXES, the shapes of the spectra reflect the detailed state for the valance electrons. One example, shown in Figure 8, is that of Au and Pt. Both spectra show a distinctive set of peaks in the 120 to 150 eV range, and additional smaller peaks in the lower energy range. These peaks have not been previously reported [2] and are believed to be the N lines for Pt and Au. In general the shapes of the two spectra are very similar, except that there is a shift of about 50 eV between the two. Although the shapes of the peaks are very similar, small differences can be noticed. These differences may reflect differences in the structure of the atoms, but still require additional investigation.

#### CONCLUSIONS

A unique wavelength-dispersive soft X-ray emission spectrometer was developed for ultralow-energy X-ray analyses. It covers the energy range between 50 eV and 210 eV. This energy range includes Li-K (54 eV), Al-L (72 eV), Si-L (92 eV), P-L (119 eV) and B-K (182 eV), but in addition, the spectrometer is very efficient at dispersing higher-order X-ray lines. As a result, X-ray lines up to 700 eV can routinely be measured. The energy reso-

lution is 0.2 eV when determined from the Fermi edge of the Al  $L$  line. This high energy resolution makes it possible to separate lines such as the N  $K$  from the Ti  $L$ , which has not been previously possible, even on traditional WD spectrometers. In addition, the WD-SXES has a very high sensitivity, making it ideal for trace element analyses of light elements. Trace element analyses of boron, carbon and nitrogen in steels can be achieved in the 10 ppm to 100 ppm range.

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#### BIOGRAPHY

Hideyuki Takahashi has a PhD in applied physics from Osaka University (1997). He is now a senior adviser to the Electron Optics Business Promotion Department at JEOL Ltd. Previously he was a manager of the application division of Electron Probe Microanalyzer and Transmission Electron Microscopy, and in the last two years, a manager of the EDS and WDS development division. He was a co-convenor of ISO202/TC2 from 2006 to 2012. He was also an editorial member of *Analytical Chemistry* in Japan. Currently he is a guest researcher at Osaka Peripheral University.



#### ABSTRACT

Wavelength-dispersive X-ray spectrometers have been around for more than 60 years. They have maintained a central role in microanalyses because of their effectiveness at measuring X-rays reproducibly, and because of their high spectral resolution. However, these traditional spectrometers have been limited in the ultralow energy range. A radically new WD spectrometer has now been developed that allows the measurement of ultrasoft X-rays, down to 50 eV. This allows for lithium to be measured into the tens of ppm range. This soft X-ray emission spectrometer (WD-SXES) uses an aberration-corrected, concave, variable line-spacing grating to disperse X-rays of different wavelengths. The dispersed X-rays then get projected onto a CCD array, which acts as the detector. The result is a solid-state spectrometer capable of collecting an entire spectrum simultaneously from 50 to 210 eV. However the grating is also very efficient at dispersing higher-order X-ray lines, and therefore lines up to 700 eV can be routinely measured.

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